



## Register of hazardous materials in printing industry as a tool for sustainable development management

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### ABSTRACT

The paper explains the concept of pollutants register. The studies are in the domain of printing industry as a relatively low source of environmental polluter, and the presented concepts, methodology and results represent the contribution to the sustainable development management. Method of data collection, compilation of the printing pollution register as well as classification of harmful substances which are emitted during the printing process is presented. Furthermore, the paper analyzes the result of the quantitative identification of hazardous substances emitted in printing industry of Novi Sad.

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### 1. Introduction

The survival of humanity is inextricably linked with the concept and emergence of sustainable development. Development as a process of work reproduction is permeated through all segments of society, and its successful implementation requires good governance, or broadly speaking good management [1,2].

In the early seventies of the 20th century, a systematic study and monitoring of pollution and environmental protection have begun. Nowadays, due to the development of management practice, there is a perceived need to provide a healthy living environment for future generations.

Life cycle assessment (LCA) is a technique for assessing various aspects associated with development of product and its potential impact throughout its life [3,4]. LCA includes definition of goal and scope, inventory analysis, impact assessment and interpretation of results [3,5–7]. The goal and scope definition describes the underlying question (objective), the system, its boundaries and the definition of a functional unit. The flows of pollutants, materials and resources are recorded in inventory analysis. These elementary flows (emissions, resource consumption, etc.) are characterized and aggregated for different environmental problems in impact assessment and finally conclusions are drawn in interpretation stage. LCA applications are comparisons of different products and systems, or different materials production or recycling methods. LCA can be used as a tool to detect potentials for improvements with the aim to reduce the impact on human health, environment and resource depletion.

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Undoubtedly, working processes within the framework of sustainable development include environmental pollution in the certain extent, and thus, particular kinds of materials and substances are the subject of environmental research. The studies that are in scope of this paper are in the domain of printing industry as a relatively low source polluter of the environment, but the presented concepts, methodology and results are the authors' contribution to the sustainable development management.

## 2. Research background

The research was carried out in the printing industry of Novi Sad, and resulted in the compilation of the polluters and pollutants register. The basics of the process are presented in the paper.

### 2.1. Pollutants register

Register of pollutants presents a list of information and data of the pollutants that are harmful to the environment and provides the basis for their monitoring and control [8–10]. It contains information about contaminants, their location, production processes, preferences and material balances of inputs and outputs of raw materials in wastewater treatment, other types of waste and landfills [9,10]. The aim of the register of hazardous materials results from the need for obtaining quality and timely information about environmental pollution released from printing facilities.

The stated objectives include:

- Identification of individual sources of pollutants.
- Reducing pollution from industrial facilities and other sources to minimum.
- Determination of the amount and trend monitoring of specific pollutants emission due to lower the risk level of adverse effects.
- Improvement of public access to information, as well as its involvement in the process of decision making on environmental issues.

The Register is an important database for decision-making and provides significant basis for preventing pollution in printing industry. It allows government agencies to identify the emission of pollutants, monitor progress in pollution prevention and thus, implement and carry out environmental policy, identify priorities and perform necessary actions towards integrated environmental protection, all in the function of sustainable development management.

The Registry is an integral part of information system for environmental protection of the Republic of Serbia, which is in direction of the Agency for Environmental Protection. It is in accordance with the Law and contains data about air and water pollution and waste management from point sources as well as the settlement, as diffuse sources [10].

The companies that should report on pollutants emission from their facility are determined by Fig. 1.

It is anticipated that operators should conduct and monitor the emissions from the facilities which are presented as the sources of emissions and environmental pollution. These obligations relate to monitoring air emissions and water pollutants, as well as waste characterization and classification [1,10]. Data collected through monitoring are submitted to the Agency for Environmental Protection in the way that is defined by the Regulations of the Republic of Serbia.

The process of data collection for the Register is shown in Fig. 2.

The Law provides civil liabilities for companies that do not monitor and track their impact on the environment and fail to provide relevant data for the Registry in the prescribed manner. According

to the Article 117 Act [10] about environmental protection, the civil liabilities for legal persons are provided if they:

- Fail to provide data about the type and amount of imported and exported substances which deplete the ozone layer, as well as about the companies and individuals who bought these substances.
- Fail to keep records about types and quantities of hazardous substances in production, transportation, traffic, use, processing, storage or disposal.
- Fail to monitor and track other impact on the environment.
- Fail to provide data relevant for integrated pollution register.
- Prevent supervision and control, i.e. fail to act according to the inspector's decision.

The Register provides an important mechanism for increasing company's responsibility, pollution reduction and promotion of sustainable development [11]. During the process of data collection for the Registry of pollutants, managers in many companies found that emissions were not only the problem of environmental pollution, but also a significant source of lost funds.

As a result of data collection from source emissions, companies started different research due to find a variety of technical and technological solutions that significantly decreased the level of impact of environmental pollution, reduced all types of emissions from the source by using alternative fuel, less hazardous chemicals and mineral resources, improved production process control and increased equipment efficiency.

### 2.2. Polluters and waste

Pollutants are found in the environment, in their natural state, as an integral part of the natural environment and living organisms, but within the limits that are harmless for life. Living organisms emit certain amount of pollutants, and it happens to all economy processes as well. However, at the low level of economic development, neutral economic conditions and in the conditions of low population density production of pollutants is low, so they are successfully degraded through natural processes. Thus, the environment, living organisms and people are unaffected. Unfortunately, due to the increase in population, urbanization of cities, economy activities and application of chemicals in industry and agriculture, nowadays, there is an excessive discharge of pollutants into the environment and its threat [12].

Polluter is a company or other natural or legal person whose activity releases polluting substances into the environment. On the other hand pollutants are the substances whose release into the environment affects its composition, properties and integrity [12].

Basically, two groups of pollutants can be distinguished: natural and anthropogenic. Bearing in mind the characteristics of natural contaminants (floods, earthquakes, volcanic eruptions) it is obvious that they are not reviewed and registered in the Registry of pollutants, but only anthropogenic pollutants. The anthropogenic pollutants are primarily divided into concentrated and dispersed contaminants.

The concentrated contaminants comprise all industrial facilities, mines, ports and docks, which have their own power, sewerage and drainage systems, clinical centers and hospitals, all villages that have power plants, waterworks and sewer system and all equipped landfills of solid and liquid waste.

The bulk contaminants comprise systems for drainage of agricultural lands, settlements without sewerage, roads, stationary and mobile traffic, septic tanks and disordered landfills of solid and liquid waste.

The term of waste includes any material or object that is created in production processes, service or other activities, items excluded

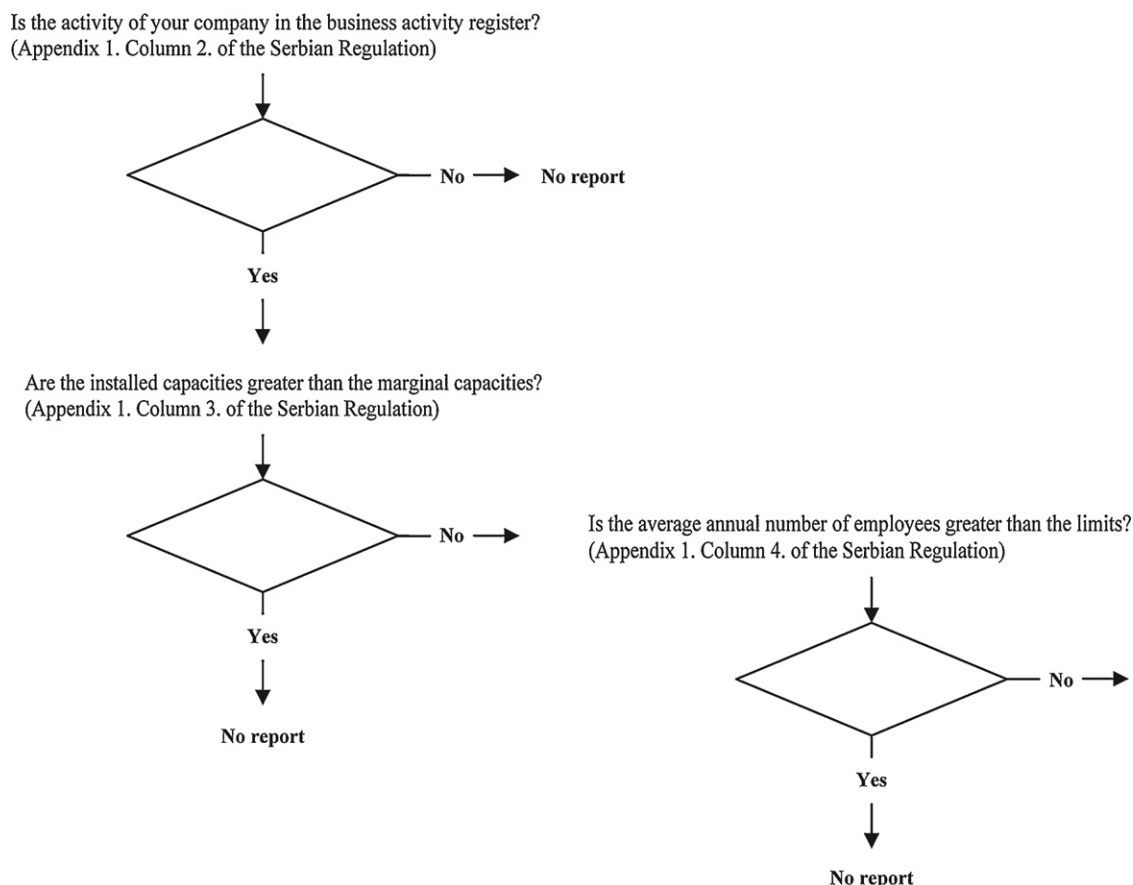


Fig. 1. Company report on pollutants emission.

from use, and waste materials generated in consumption and that in terms of producers or consumers is not for further use and must be disposed [13]. Waste can be classified as hazardous, non-hazardous, inert, municipal, domestic, commercial, biodegradable, packaging and industrial.

Waste management considers implementation of prescribed measures for waste collection, transportation, storage, treatment and disposal, including the supervision of these activities and care of facilities for waste management after the closing. Waste disposal is done in special courts with reference to the geological, hydrological, topographical, climate conditions and distance from settlements. In the Republic of Serbia the only way to manage waste disposal are local landfills, but unfortunately, with very few exceptions, they fail to meet even the basic sanitary, technical and technological standards [14].

### 2.3. Printing industry as a polluter

Printing facility provides a wide range of waste material that is harmful to the environment and people. In order to facilitate consideration of the technological process and its impact on the environment, the flow diagram of process is made (Fig. 3).

In the printing industry as well as in other industries there is a rough classification of pollutants: solid, liquid and gaseous wastes. Solid waste in the printing industry includes the following: empty containers, canisters, materials that have expired, damaged plates, developed film and paper waste. The liquid waste include lubricating oils, waste paint, solvents for cleaning, film developing chemicals, acids, bases, and metals such as silver, iron, copper, chromium and others. Printing processes produce volatile organic compounds and pollutants emitted mainly by using the cleaning

agents, inks, and alcohol and other solutions for the dampening of printing plates. All this represents the gaseous waste from the printing industry.

The hazardous waste generated in the printing industry consists of:

- Packaging which contains residues of hazardous substances, or the dirt with dangerous materials (inks, solvents, cleaning solutions).
- Developer and activator.
- Waste containing silver.
- Rinse aid, rags and other absorbent materials for washing and cleaning which contains dangerous substances.
- Waste inks, varnishes, printing cartridges.
- Sledges containing inks, varnishes and other pollutants.

Printing industry effluents are shown in Table 1.

Almost every manufacturing process is a source of wastewater with certain characteristics. Wastewater in the printing industry is present in the conventional preparation of printing plates (prepress process), in the process of offset printing, as well as in cleaning printing machines. Silver compounds, used developer, fixer and chromic compounds of chemicals for cleaning are released into water during the process of prepress. Thus, the waste from the printing process can be defined as hazardous waste.

Iron, copper, chromium and nickel in the water flow will cause its accumulation in aquatic organisms which will continue to increase in the food chain and therefore the man as a consumer of such water may be seriously endangered. If metal concentrations exceed the maximum allowable amount, the metal will act as a toxicant. The amount and composition of wastewater in the

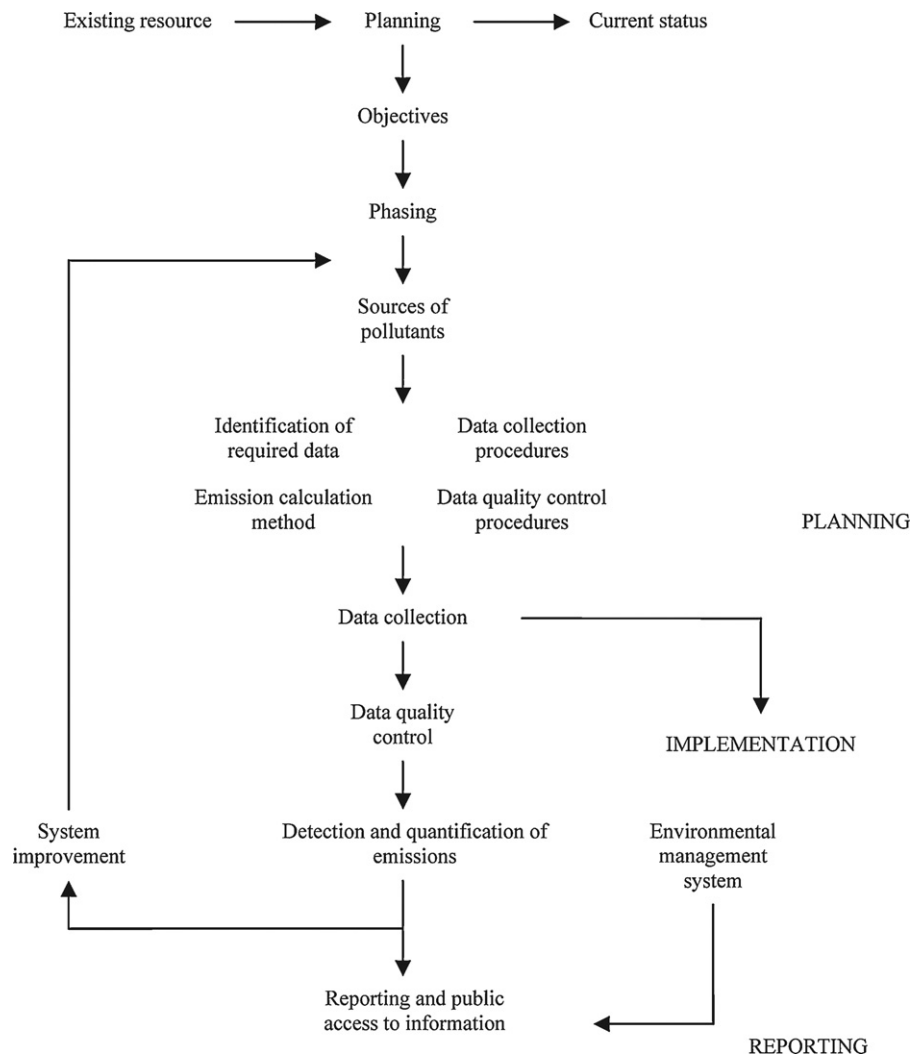


Fig. 2. Data collection for the Register of pollutants.

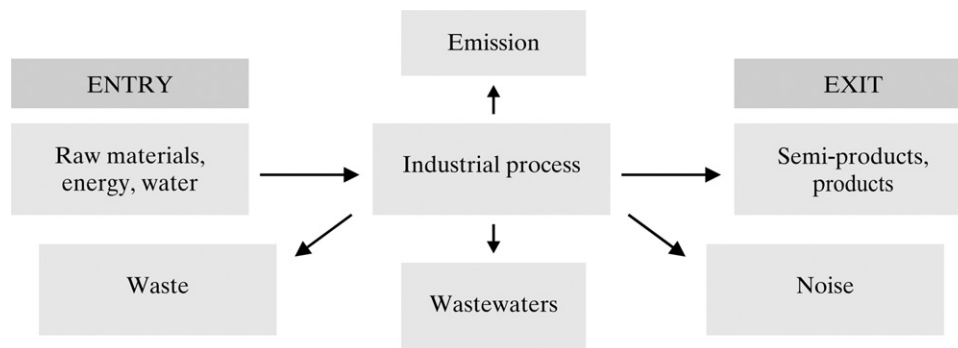


Fig. 3. General flowchart diagram of the industrial production process.

preparation of printing plates depends on the process of developing as well as flushing fluid.

Pollutants emitted in the printing process are related primarily to the chemical composition of the inks used in different printing processes, and then to all auxiliaries such as solvents for washing machines and inking units, fountain solutions for offset printing process, etc. Each process is characterized in its own way and each production process has certain characteristics of wastewater. Wastewater in the printing industry as well as released toxic substances differs from process to process.

Application of isopropanol in the fountain solution for offset printing process sets off the emission of pollutants from VOC group (volatile organic compounds). Short-term exposure to VOCs can cause eye irritation and respiratory tract inflammation, headache, dizziness, visual disturbances, fatigue, loss of coordination, allergic skin reactions, nausea and memory impairment. However, extended exposure could lead to disastrous consequences. When using the tool for moisture with unfavorable characteristics it is necessary to consider the consequences and the amount of harmful substances in the wastewater [15].

**Table 1**  
The effluents of printing industry.

Parameter	MAC (mg/l)
pH	6.5–10
BOD	30
COD	150
TSS	50
Oils and lubricants	10
Chromium hexavalent	0.1
Total	0.5
Copper	0.5
Silver	0.5
Zinc	2

BOD, biological oxygen demand; COD, chemical oxygen demand; TSS, total suspended solids.

Three different types of inks are used in flexographic printing technique, i.e. inks based on organic solvents, water based inks or UV inks. Organic solvents from the inks are volatile organic compounds and their application in the printing process is a health and safety risk in terms of air pollution at the workplace. In the outer atmosphere these solvents participate in photochemical reactions. Inks that are dried by UV radiation are composed of monomers, photoinitiators, pigments and additives. Monomers and oligomers are well known for their irritant effect on the skin, and a source of UV radiation emits ozone which also reflects the negative side of using these inks.

Pollution in the screen-printing begins with the development of copying layers based on gelatin, polyvinyl alcohol or polyvinyl acetate or dichromate sensitized diazo-compounds. Due to reduce the pollution it is important to avoid the copier-based dichromate, inks containing heavy metals, dyes with organic solvents, chemicals containing hypochlorite.

Electromechanical engraving, which is used in conventional prepress process for gravure printing, is environmentally favorable. However, corrections and chrome has a disadvantage, especially expressed in chrome. According to the list of waste materials waste chromium plating bath is toxic and thus, it should be collected, transported and disposed in the special way [15].

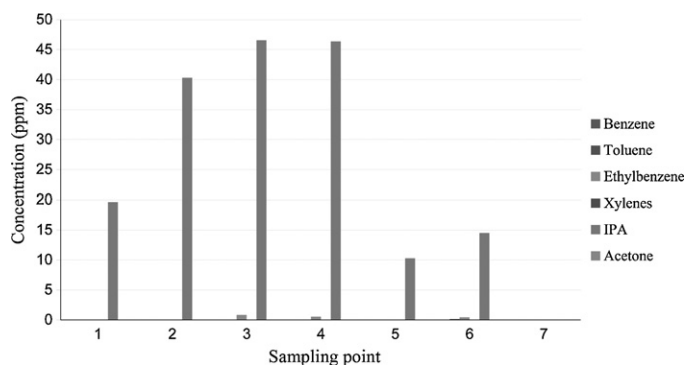
The most of cleaning agents is obtained from oil but the worst is petroleum as very volatile and flammable substance. In the working environment these substances are health and safety risk (flammability class of these substances is A1, AII and AIII). Outdoors they enter into chemical reactions and result in photo-oxidant compounds and cause smog. The laundry facilities should meet certain requirements: ignition temperature should be above 55 °C, it may contain aromatic compounds in the proportion less than 0.1%, without substances that are health risk and items with iodine number above 20 [15].

### 3. Research results

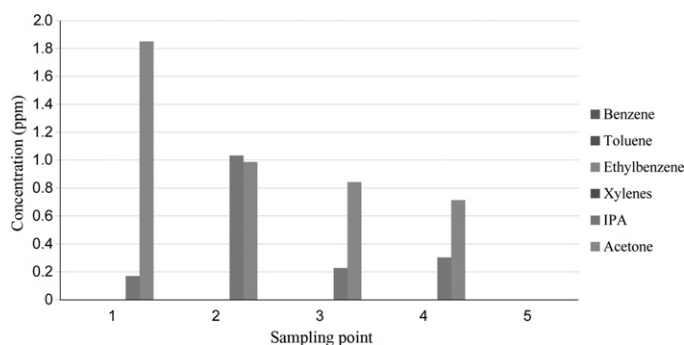
#### 3.1. Quantitative identification of hazard in printing industry of Novi Sad

Based on the data collected in the field and classified in the real conditions of selected printing facilities operation, the appropriate substitution of the individual toxic substances in the mixtures of solvents are proposed with eco-friendly solvents, whose physical and chemical characteristics have benefit impact on profitability and efficiency of the technological processes, as well as on the quality of living and working environment [16,17].

Quantitative analyses of the presence of certain pollutants were carried out by using different physical and chemical methods and instruments: mobile gas chromatograph Voyager, Photovac, Inc., portable ozonometer Aeroqual Series 200, Aeroqual Ltd., mass



**Fig. 4.** Dependence of VOC concentrations on the sampling point in offset printing facility X.



**Fig. 5.** Dependence of VOC concentrations on the sampling point in digital printing facility Y.

spectrometer Perkin Elmer Elan 5000 with inductively coupled plasma and sound level meter TES-1358A with RS-232 interface [18–31].

Real-time measurements of BTEX, isopropanol, acetone and formaldehyde concentrations were performed in the offset (X) and digital (Y) printing facilities in Novi Sad, Figs. 4 and 5. Concentration data of target VOCs were obtained promptly, registering current situation and status of the working environment. Concentration levels of target VOCs in offset and digital printing facilities (55.72 ppm) are within the framework of the permissible exposure limit (PEL) for 8-h time-weighted average (TWA) recommended by the Occupational Safety and Health Administration (OSHA) [18–20].

The concentrations of formaldehyde were measured in the offset printing facilities of Novi Sad during the printing process [20]. The average values of formaldehyde concentrations were in the range from  $1.70 \pm 0.01$  to  $6.75 \pm 0.01$  ppm for the all offset printing facility ( $X_1$ ,  $X_2$ ,  $X_3$  and  $X_4$ ) (Fig. 6). It is evident that the average concentrations of formaldehyde in printing facility  $X_3$  are below 2 ppm, which is prescribed by the OSHA. The average value of formaldehyde concentrations in all the printing facilities was  $5.03 \pm 0.01$  ppm, which is much more above the OSHA standard.

Variations in the formaldehyde concentrations in offset printing facility are related to the chemical compositions of raw materials, ambient conditions, and distance from the printing machine, as well as type of air filtration system installed in the printing machine [20].

Experimental results showed that ambient ozone concentrations raise with the increase of total volatile organic compounds (TVOCs) concentration and intensive use of UV lamps during digital and screen printing process [21–23]. The ozone concentrations were much above the PEL for 8-h TWA recommended by the OSHA, unlike to the TVOCs concentration. The maximum allowed concentration (MAC) of ozone emission in workplace air is 0.05 ppm,



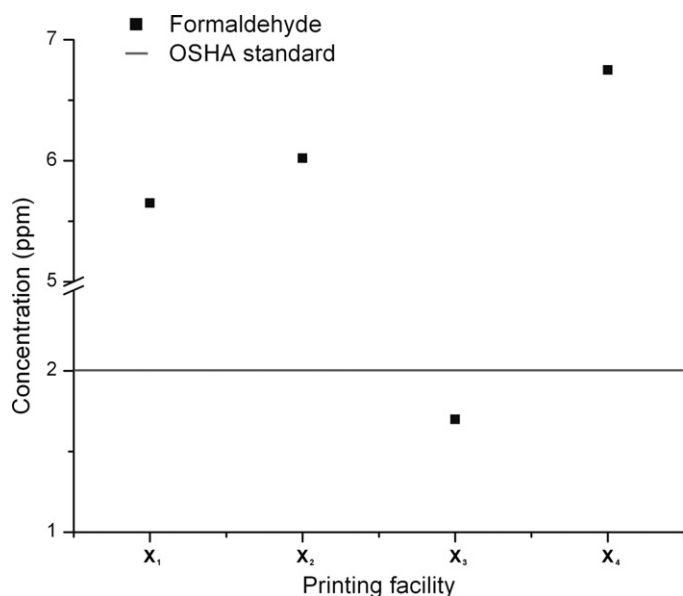


Fig. 6. The average concentrations of formaldehyde measured in four representative offset printing facilities.

according to the Serbian Regulation. It was observed that the ozone concentrations varied depending on the type of screen-printing process. The average ozone concentrations were in the range from 0.12 to 0.45 ppm and 0.81 to 0.92 ppm in semi-automatic and automatic printing process, respectively.

Digital printing machine PressVu UV equipped with UV lamps produces high quantity ambient ozone during the printing process [21,22]. Therefore, the ozone concentration levels decrease dramatically when the machine is in standby mode (Fig. 7). On the contrary, textile-printing machine, Teleios, produces lower concentration levels of ozone during ink fixation than PressVu UV machine, which is insignificant during the printing process (Fig. 8).

Distribution of persistent organic pollutants (POPs) between the gaseous and particulate phase in ambient air was estimated using the experimental values of POPs concentrations in 129 air samples from 24 selected settings in urban, industrial and “background” sites [24–26] (Fig. 9).

The liquid waste of printing industry contains large amounts of organic substances such as oil-based inks, developer, fixer, varnishes, solvents, binders and others. The largest sources of water recipients pollution are printing inks especially azo-dyes, which

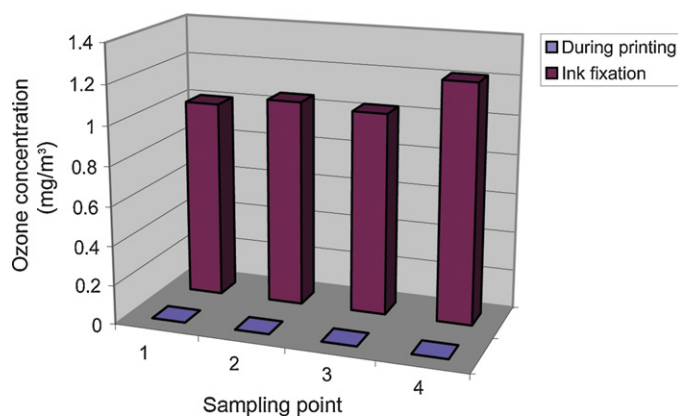


Fig. 8. Concentration levels of ozone on printing machine Teleios.

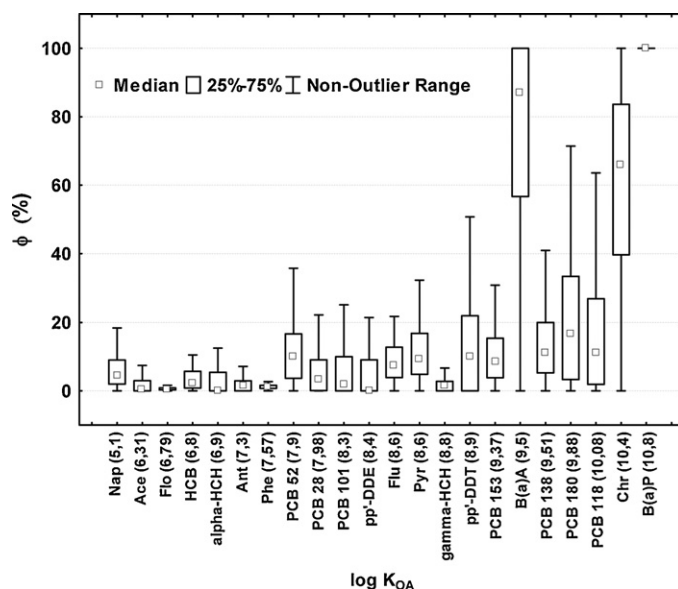


Fig. 9. Variability of the particle-bound fraction  $\phi$  (%) for the selected POPs in the collected samples of ambient air.

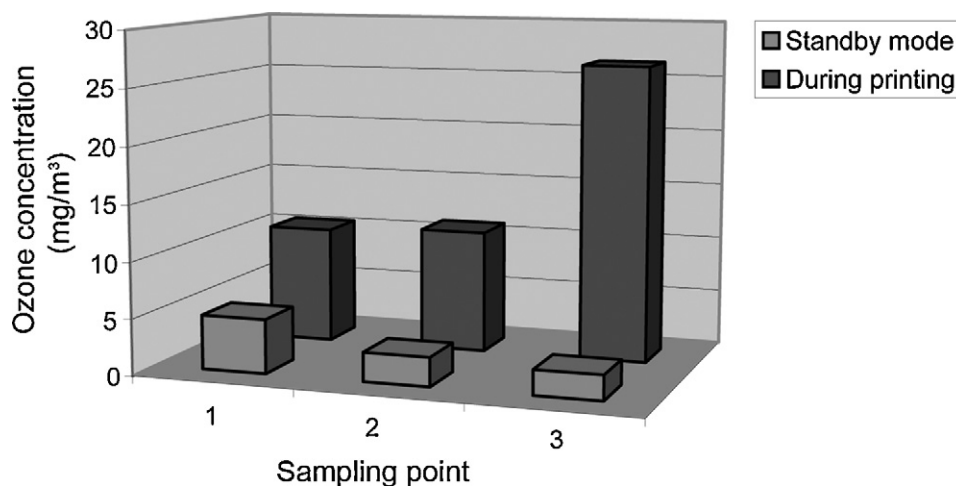
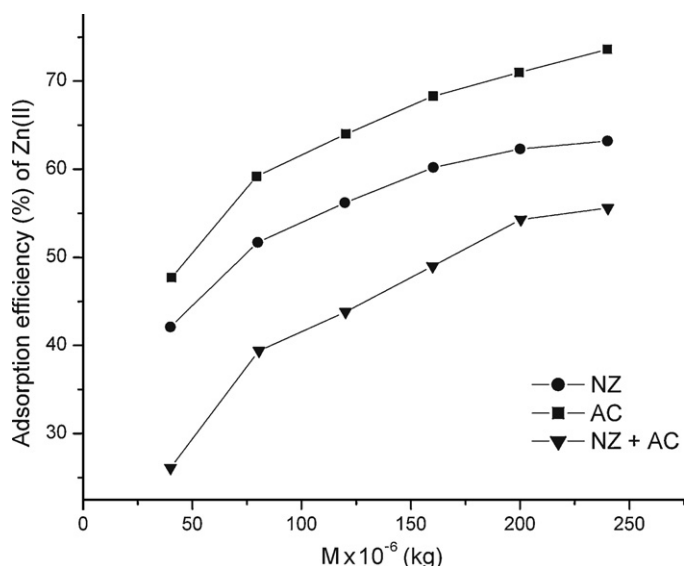
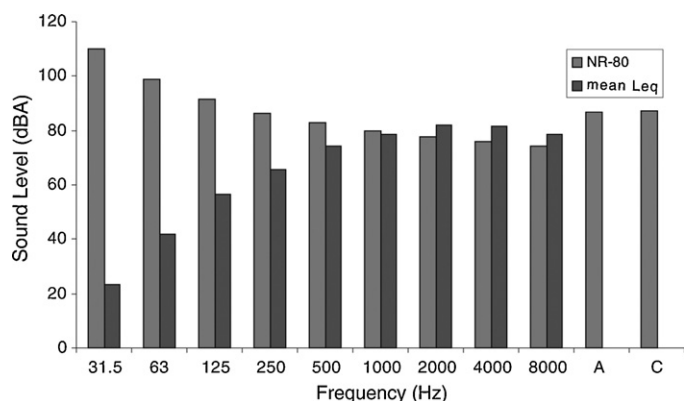


Fig. 7. Concentration levels of ozone on printing machine PressVu UV.

**Table 2**

Concentration levels of Zn(II) ions in printing developer before and after adsorption.

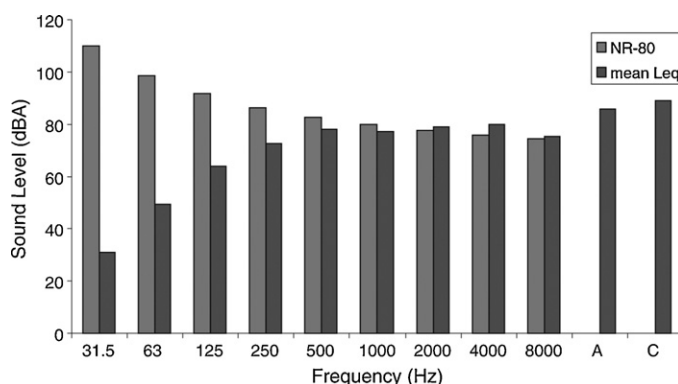
Concentration (mg/l)				
Before adsorption		After adsorption		
Fresh developer	Spent developer	AC <sup>a</sup>	NZ <sup>a</sup>	NZ + AC <sup>a</sup>
1.278 ± 0.064	17.302 ± 0.865	6.233 ± 0.312	7.624 ± 0.381	9.567 ± 0.478

<sup>a</sup> Spent printing developer after adsorption on AC, NZ and NZ + AC.**Fig. 10.** The influence of the adsorbent amount on the adsorption efficiency of Zn(II) ions.**Fig. 11.** The noise levels from folding unit in printing facility X.

are the most toxic among the all commercial inks. The problem of printing wastewater pollution is solved by adsorption onto natural low-cost adsorbents such as zeolite-clinoptilolite (NZ), activated carbon (AC) and their mixture (NZ + AC) [27,28]. The efficiency of printing wastewater purification is accompanied by immobilization of metal ions during the contact time. The results showed the efficiency of adsorbents in the following order: AC > NZ > NZ + AC (Table 2 and Fig. 10) [27,28].

The level of noise, as psychological and physical pollutant, was measured in the offset printing facility. It was observed that the highest level of noise is produced by offset printing machines and folding units [29–31]. The level of noise considerably increases with faster mode of offset printing machine and compressor (Fig. 11).

Measurements showed that the level of noise in offset printing facility X does not exceed the permitted level according to the

**Fig. 12.** The level of noise of offset printing machine in printing facility X.

Regulation of the level of noise in environment of 75 dBA (Fig. 12), which means that there are printing facilities that have successfully solved the problem of noise pollution.

#### 4. Conclusion

This paper demonstrated the process of creating database of hazardous substances in the printing industry of Novi Sad as a background of sustainable development management, and thus, Novi Sad and the Republic of Serbia successfully satisfied a part of the imposed conditions for European integration.

Printing industry can significantly affect the environment responsible disposal of the produced waste with relatively low cost, whether through the individual segments of the printing production or the entire production process.

The results of the investigation showed that:

- There is a possibility of the removal of heavy metal ions as significant hazard from the printing wastewaters and liquids by activated carbon, zeolite and their mixture.
- The concentration levels of detected VOCs are within the framework of the PELs for the 8-h working time of 55.72 ppm.
- The distribution of persistent organic pollutants between the gaseous and particulate phase in ambient air is estimated by using experimental values of POPs concentrations for urban, industrial and “background” sites.
- The printing machine (Leq = 82.70 dBA) and folding unit (Leq = 87.66 dBA) produce the highest noise level.

Based on the obtained experimental data, the Register of pollutants of printing facilities on the territory of Novi Sad was drawn up.

#### Acknowledgements

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